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Soft Nondamaging Contacts Formed from Eutectic Ga–In for the Accurate Determination of Dielectric Constants of Organic Materials

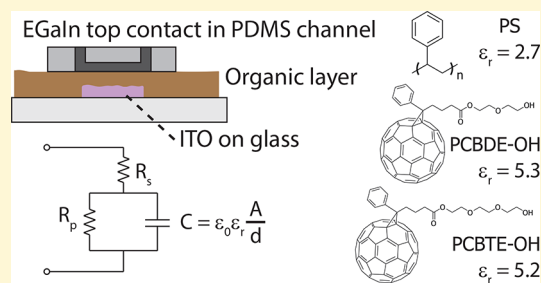
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Supporting Information

ABSTRACT: A method for accurately measuring the relative dielectric constant (ϵ_r) of thin films of soft, organic materials is described. The effects of the bombardment of these materials with hot Al atoms, the most commonly used top electrode, are mitigated by using electrodes fabricated from eutectic gallium–indium (EGaIn). The geometry of the electrode is defined by injection into microchannels to form stable structures that are nondamaging and that conform to the topology of the organic thin film. The ϵ_r of a series of references and new organic materials, polymers, and fullerene derivatives was derived from impedance spectroscopy measurements for both Al and EGaIn electrodes showing the specific limitations of Al with soft, organic materials and overcoming them with EGaIn to determine their dielectric properties and provide realistic values of ϵ_r .



INTRODUCTION

Years of theoretical and experimental studies have established design rules to control many bulk properties of organic materials (e.g., bandgaps). Mechanical, optical, and electrical tuning can successfully be done synthetically by choosing the right pendant group or atom to incorporate on the backbone of a conjugated polymer, oligomer, or a small molecule. However, one of the most important properties of these materials, the relative dielectric constant (ϵ_r), which is well studied and known for inorganic materials, remains difficult to control and characterize for organic materials. To build a bridge between theory and measurements, we need a fast and precise method of deriving ϵ_r specifically for soft, organic materials. There are many techniques for measuring ϵ_r , which can be classified in different groups, namely, free space methods, transmission line, and resonant. Each type of technique imposes different limitations on the measured frequency range and the type of material. Most of these techniques work well with (hard) inorganic materials, liquids, and malleable solids but require large amount (grams) of the tested materials.^{1–5} With the discoveries of new, organic materials, which are typically initially developed using milligram-scale synthetic routes, versatile methods of characterization are needed.

In recent decades, there has been a lot of interest in semiconductors made from organic materials such as conjugated polymers, fullerene derivatives, and other small molecules for applications in organic electronics, e.g., organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs).^{6–9} More recently, ϵ_r of organic materials has emerged as a useful synthetic goal, due in part to the theoretical and modeling

work of Koster et al. predicting that power conversion efficiencies (PCEs) of more than 20% can be achieved by taking into account an increased ϵ_r up to 10.¹⁰ A few approaches to the design of organic molecules for OPVs have been studied to achieve increased ϵ_r in pursuit of higher efficiencies, since most of the commonly used organic materials exhibit a ϵ_r of 3–4. These approaches include the introduction of high- ϵ_r dopants (small molecules or ions^{11,12}) or the modification of the molecular structure such that the materials inherently demonstrate a higher dielectric constant preferably without any change on other electrical or optical properties.^{13–15} The latter approach focuses more on the introduction of pendant groups that are highly polarizable or that exhibit high dielectric constants on conjugated polymers and fullerene derivatives, such as cyano and nitrile groups or the addition of fluorine atoms. However, to date relatively few materials have been synthesized and their dielectric properties carefully measured. High values of ϵ_r were observed for polymers (from 3.5 to 5.0) and fullerene derivatives (from 3.9 to 4.9) bearing cyano groups, while larger increases were observed with the addition of oligoethylene glycol (OEG) side chains.^{13,16} Polymers with OEG chains exhibit values of $\epsilon_r \leq 6.3$, which is among the highest reported in the literature so far for conjugated polymers.¹⁷ The synthesis of new organic materials is slow and resource intensive; months or years of effort often result in only a few milligrams of testable material. Thus, an experimental method of measuring ϵ_r that requires

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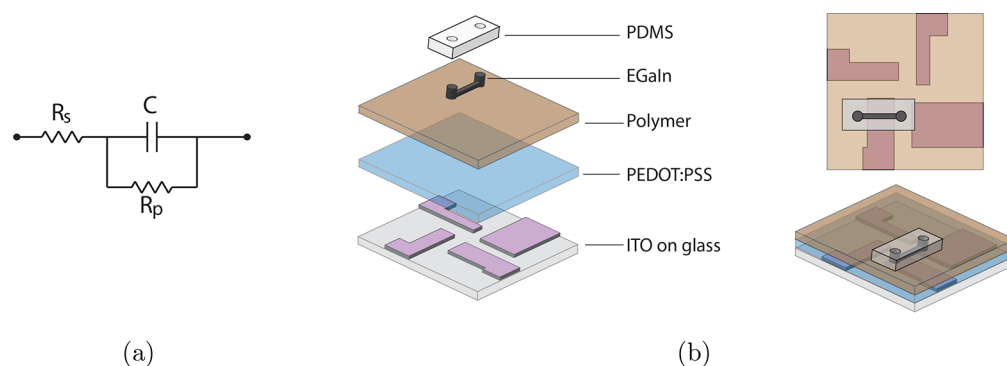


Figure 1. (a) Equivalent circuit used for fitting impedance data. R_s represents the series resistance (in the range of Ω) due to plate resistance and probe effects. The parallel resistance (R_p , in the range of $M\Omega$) is needed to account for the finite resistance of real dielectric materials, and C represents an ideal capacitor. (b) Device architecture with EGaIn as the top electrode. In lieu of a vapor-deposited metal electrode, a PDMS channel is placed on top of the film and filled with EGaIn.

grams of material is a bottleneck in the development of synthetic methodologies and design rules to control ϵ_r . An apt comparison is bandgap engineering, where proof of concept of the optical tuning of organic materials can be achieved with a UV–vis measurement, which requires <10 of material and only a few minutes to complete. A comparably precise, fast, and reliable method for providing experimental feedback on ϵ_r to synthetic efforts does not currently exist.

A commonly used technique for determining ϵ_r , which is similar to the transmission line technique, is to measure the dielectric response of devices using impedance spectroscopy (IS). A thin film of the material under study is sandwiched between two planar electrodes and subjected to a small perturbation of low-amplitude ac signal with sweeping frequency.^{12,15,18} This method allows measurements on milligram quantities of (organic) materials, obviating gram-scale synthetic routes for measuring ϵ_r . To derive the capacitance (from which ϵ_r is determined), an equivalent electric circuit of a real capacitor consisting of a series resistance, a parallel resistance, and an ideal capacitor, as shown in Figure 1a, is used for fitting the data.

The impedance of an ideal capacitor is

$$Z_c = \frac{1}{j\omega C} \quad (1)$$

such that the total impedance of the circuit in Figure 1a would be

$$\begin{aligned} Z &= R_s + \frac{R_p}{1 + j\omega R_p C} \\ &= R_s + \frac{R_p}{1 + \omega^2 R_p^2 C^2} - j \frac{\omega R_p^2 C}{1 + \omega^2 R_p^2 C^2} \\ &= Z' + jZ'' \end{aligned} \quad (2)$$

where Z' is the real part and Z'' is the imaginary part of the impedance of the circuit. Fitting the acquired data from IS in eq 2, one can calculate R_s , R_p , and C with their errors. Knowing the capacitance, the area of the device, A , and the thickness, d , one can derive ϵ_r from

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (3)$$

where ϵ_0 is the absolute dielectric permittivity.

The typical device used for IS measurements is similar to bulk heterojunction (BHJ) OPV devices, consisting of a glass substrate with four ITO areas acting as bottom electrode, a PEDOT:PSS layer, a spin-cast layer of the material under study, acting as dielectric, and four evaporated aluminum (Al) contacts as top electrodes. Unfortunately, deriving ϵ_r for organic semiconducting materials is not as streamlined as, for example, an NMR measurement. Fabricating films of organic materials by spin-coating can be difficult to control, particularly the surface roughness of the film on which Al will be deposited. This lack of control, unfortunately, does not always guarantee that the deposition of Al will exactly follow the surface of the film and can result in nonplanar, parallel electrodes, the assumption of which is necessary to use eq 3 to derive ϵ_r ; rough films lead to an overestimation of ϵ_r .¹⁹ Additional difficulties arise from the over- or underestimation of d since dents or bumps on the surface—which do not necessarily average out—will change its value locally. Another issue that arises is that Al must be deposited through thermal (or e-beam) deposition *in vacuo*, which exposes the organic film to heat and energetic metal atoms. Because the organic materials tend to be soft (compared to their inorganic counterparts), delicate, and redox active, the influence of Al on the capacitance of the device could be crucial to the extraction of the correct value ϵ_r . For example, the deposition of Al/LiF contacts leads to the unintentional doping of thin films of fullerene derivatives, resulting in an overestimation of ϵ_r by about a factor of 2.²⁰

We propose eutectic Ga–In (EGaIn) as an alternative electrode to Al for the accurate determination of ϵ_r in soft and otherwise delicate (organic) and/or scarce materials. EGaIn is an inexpensive, commercially available eutectic alloy with a mp of 15.5 °C.²¹ Upon exposure to air, a self-limiting 0.7 nm thick layer of highly conductive Ga₂O₃ forms, which imparts shear-yielding rheology.²² (The capacitance of β -Ga₂O₃ is on the order of nF, which will have a negligible impact at the thickness and conductance of the disordered Ga₂O₃ that forms spontaneously, assuming that it even remains intact.²³) Along with its high electrical conductivity (3.4×10^4 S cm^{−1}), the unique rheology of EGaIn makes it an excellent candidate for a top electrode making soft, electrical contacts because it can be molded by soft lithography, while still conforming to surfaces.²⁴ It has already been extensively studied as a top-contact for forming tunneling junctions comprising self-assembled monolayers (SAMs) as shown in previous

studies.^{21,25–30} EGaIn contacts can be formed at room temperature and are unreactive and nondamaging, avoiding any steps requiring low pressure or high temperatures that may damage the organic layer (e.g., as does LiF) while still conforming to the surface topology like a vapor deposited contact.^{24,31} To prepare electrodes for IS, EGaIn is simply injected into preformed polydimethylsiloxane (PDMS) microchannels with the desired architecture for contacting the organic layer as is shown in Figure 1.^{24,32,33}

Impedance spectroscopy measurements with EGaIn have already been reported for SAMs, which are far more fragile than thin-films of organic materials,³⁴ to calculate R_s , R_p , and C ; the results were in accordance with previously reported values.^{35,36} In this work, substrates form a series of organic materials, polymers and fullerene derivatives (Figure 2) were

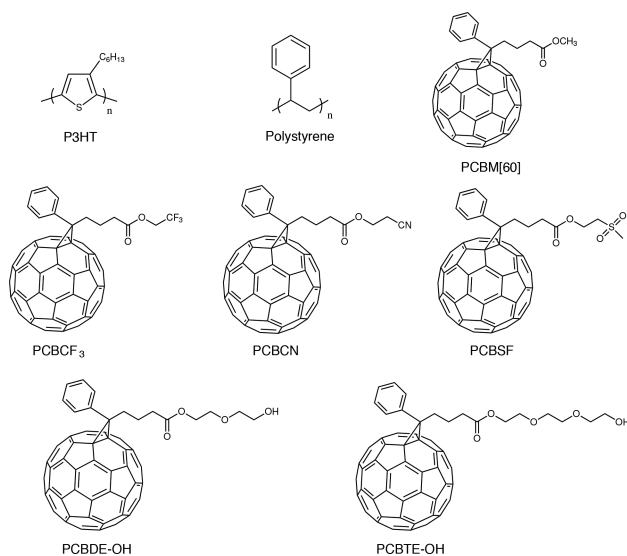


Figure 2. Structures of fullerene derivatives and polymers that were used for impedance spectroscopy measurements with aluminum and EGaIn as top electrodes.

fabricated, and IS measurements with two different electrodes (Al and EGaIn) were performed to investigate their dielectric properties. The device architecture is shown in Figures S1 and S2.

RESULTS AND DISCUSSION

Poly(3-hexylthiophene-2,5-diyl) (P3HT) and phenyl- C_{61} -butyric acid methyl ester ([60]PCBM) are among the most commonly used and well-studied materials for organic electronics, particularly OPV devices.^{37,38} Both of them exhibit low values of $\epsilon_r = 3.0$ for P3HT and 3.9 for PCBM.^{13,39,40} Impedance spectroscopy measurements were performed with Al and EGaIn as top electrodes to verify their dielectric properties. The Nyquist and Bode plots along with the capacitance plotted over frequency are shown in Figure 3. The Bode plot shows the dependence of $|Z|$ on frequency, while the Nyquist plot (inset) shows the behavior of a real capacitor with the shape of a semicircle. For P3HT the dielectric constant for both Al and EGaIn $\epsilon = 3.3 \pm 0.1$ and for PCBM 3.9 ± 0.1 , which are in accordance with the values reported in previous literature.³⁹ Although the capacitance differs between Al and EGaIn top electrodes across most of the frequency range in Figure 3, the areas of the two electrodes differ, giving rise to similar values of ϵ .

As can be seen in Figures 3a and 3c, the capacitance of P3HT and PCBM drops for frequencies higher than 10^4 Hz with Al contacts, while with EGaIn contacts, the capacitance is almost independent of frequency. This transition frequency (f_T , where $|Z|$ drops by 10%) for low values of R_s (on the order of 10Ω) is observed at very high frequencies—outside the range accessible by the instrument—making the capacitance frequency independent. With higher values of R_s (on the order of 100Ω), f_T shifts to lower frequencies (10^4 – 10^6 Hz).

The frequency independence of capacitance with EGaIn contacts can also be seen in the Bode plots (Figure 3b,d, $|Z|$, black square over frequency) where the effect of R_s is observed at the rightmost plateau of the plot for the case of Al (Figure S3), while for EGaIn it is a straight line with a negative slope (Figure 3b,d). Avoiding this abrupt drop in the capacitance, we gain more data points from which we can derive C (eq 3) with higher precision.

To validate the results from EGaIn further, we tested another reference material, polystyrene (PS, Figure 2), a well-studied material with an established value of $\epsilon = 2.6$ (at 25°C , 1 kHz – 1 MHz).⁴¹ The capacitance over the frequency is plotted in Figure 4a for Al and EGaIn as top electrodes. These data yielded values of $\epsilon_r = 2.6 \pm 0.1$ for Al and 2.7 ± 0.1 for EGaIn, both in agreement with the literature values within the error margin. (See the Supporting Information for an explanation of the uncertainty of ± 0.1 .) Moreover, the frequency response of PS exhibits similar behavior as P3HT and PCBM, showing a higher transition frequency for EGaIn than Al near the end of the measured range. Devices with Al contacts also produce higher values of R_s than EGaIn contacts. One could argue that lower R_s are achieved due to a smaller effective electrode area with EGaIn compared with Al. This explanation, however, is ruled out by the observation of similar values of capacitance for comparable areas (a_1 of Al and a_4 of EGaIn, Figure S10) of electrodes in which devices using EGaIn showed lower R_s than those using Al.

Having established that EGaIn electrodes produce the same value of ϵ_r for the reference materials—including PS, the dielectric properties of which are particularly well-defined—we measured the dielectric properties of a series of fullerene derivatives bearing different pendant groups that should effect ϵ_r .

Devices from PCBCF₃, a fullerene derivative bearing a trifluoromethyl group, with varying film thicknesses, were fabricated with the two different electrodes. Capacitance and impedance plots are shown in the Supporting Information. The values of $R_s \approx 100 \Omega$ for Al and $\sim 10 \Omega$ for EGaIn, following the same trend described above. The calculated values of $\epsilon_r = 4.2 \pm 0.1$ for Al and 4.3 ± 0.1 for EGaIn, i.e., both methods giving the same value within error. The dielectric constant of PCBCF₃ is comparable to the value of PCBM, a low-dielectric material, as expected due to the low polarizability of the C–F bond.⁴² As discussed by Hougham et al., in the case of $-\text{CF}_3$, although there is a decrease in the electronic polarization that could lower the dielectric constant, the commensurate increase of the dipole orientation overcompensates. As a result, there is little overall change in the dielectric constant.⁴³ That interplay could explain the slightly increased ϵ_r of PCBCF₃ compared to PCBM.

Recently, materials with oligoethylene glycol chains (OEG) have drawn interest due to the increased value of ϵ_r for fullerenes and polymers bearing them. It has been shown that they not only increase the polarity but also provide a higher

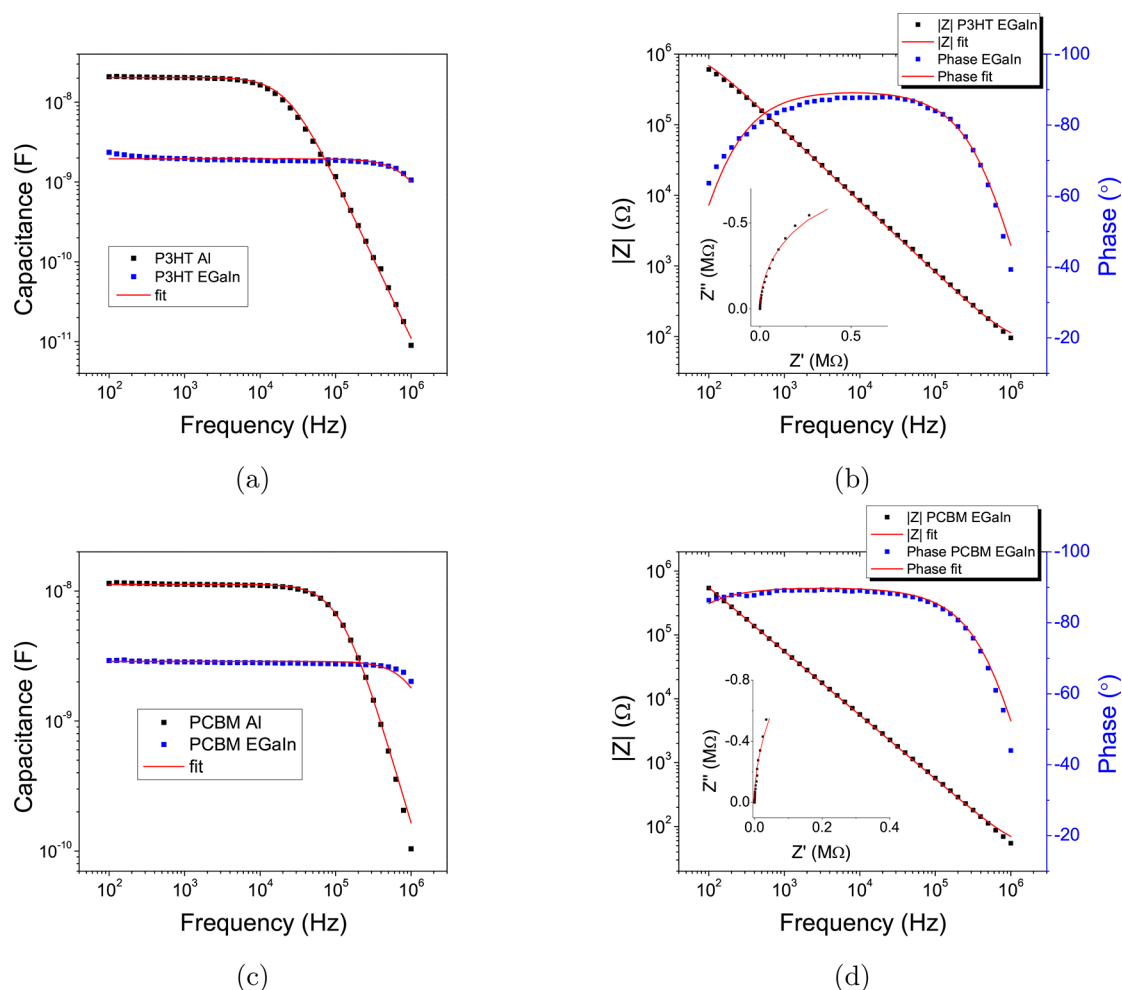


Figure 3. Capacitance versus frequency plots for (a) P3HT and (c) PCBM films with Al and EGaln electrodes and (b) and (d) Nyquist and Bode plots of a P3HT and a PCBM device, respectively, with EGaln as top electrode. The measured data of the magnitude ($|Z|$, black squares) and the phase (blue squares) are plotted against the frequency, while the red lines represent the fit over the measured data. In the inset, the Nyquist diagram of the device is plotted showing the behavior of a real capacitor.

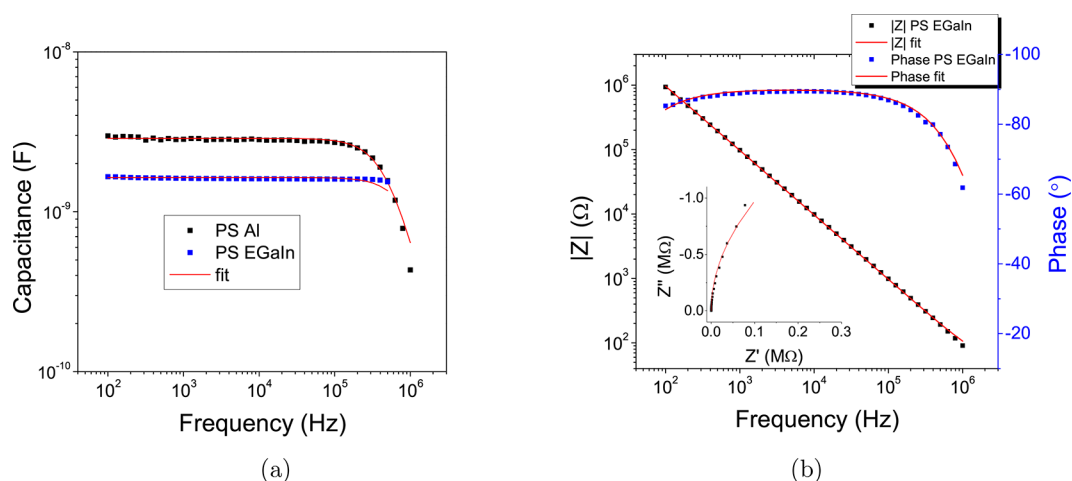


Figure 4. Capacitance versus frequency plots for (a) PS film with Al and EGaln electrodes and (b) Nyquist and Bode plots of a PS device with EGaln as top electrode. The measured data of the magnitude ($|Z|$, black squares) and the phase (blue squares) are plotted against the frequency, while the red lines represent the fit over the measured data. In the inset, the Nyquist diagram of the device is plotted showing the behavior of a real capacitor.

chain flexibility.^{16,18,44} We synthesized two fullerene derivatives bearing two (PCBDE-OH) and three (PCBTE-OH) ethylene

glycol units with a terminal hydroxyl group. Both materials exhibited higher ϵ_r values compared to PCBM and lower R_s for

the EGaIn devices as can be seen from the Bode and capacitance plots (see the [Supporting Information](#)). The values of $\epsilon_r = 5.0 \pm 0.1$ for PCBDE-OH using Al and 5.3 ± 0.1 using EGaIn. The same trend was found for PCBTE-OH; $\epsilon_r = 5.0 \pm 0.1$ using Al and 5.2 ± 0.1 using EGaIn. Both materials showed increased ϵ_r compared to PCBM attributed to the OEG chains.

We also examined PCBSF, a fullerene derivative bearing a sulfone group, which is a small, dipolar group with high dipole moment (5 D) that was incorporated in the glassy polymer poly(2-(methylsulfonyl)ethyl methacrylate) (PMSEMA) to achieve a value of $\epsilon_r \approx 12$, which is quite high compared to most organic materials.⁴⁵ We synthesized PCBSF and fabricated devices with the different electrodes to investigate the dielectric properties imparted to small molecules by sulfones. In this case, devices with different electrodes gave significantly different numbers for ϵ_r : 3.9 ± 0.1 using Al and 5.1 ± 0.1 using EGaIn. After annealing at 170 °C for 6 min before depositing the electrodes, $\epsilon_r = 5.3 \pm 0.1$ using Al and 5.4 ± 0.1 using EGaIn, putting them within the same range of difference as the other materials. To control for the effect of annealing, we measured all of the materials after annealing and compared the results. There was no impact on ϵ_r for the other materials, which implies that the effect is related to the presence of sulfones. Franklin et. al observed an improvement in the performance of field-effect transistors that use printed EGaIn contacts after annealing that was strongest when the annealing step took place before the deposition of EGaIn.⁴⁶ While it is not possible to draw any firm conclusions from this comparison, they also speculate that the effect is related to surface interactions and the interface with EGaIn.

Lastly, we examined another strong polar group that has attracted some attention as a candidate to increase the dielectric constant of organic materials, the cyano group. In polymers, specifically in polyimides, the incorporation of cyano groups increased ϵ from 3.1 to 3.8, while in fullerene derivatives, a series of cyano-functionalized fullerenes exhibited $\epsilon_r \approx 4.9$.^{14,15} To explore the effect of the cyano group further, we synthesized PCBCN (Figure 2). The resulting capacitance over frequency plots reveal a difference of R_s between devices, with EGaIn contacts giving lower values together with an increase in the capacitance at low frequencies. The values of $\epsilon_r = 4.1 \pm 0.1$ using Al and 5.1 ± 0.1 using EGaIn.

The results of the dielectric constant measurements are summarized in Table 1. For the reference materials, P3HT, PCBM, and PS, the calculated ϵ_r for EGaIn was in accordance with literature values. All of the devices using EGaIn also showed lower values of R_s , rendering the capacitance

frequency-independent across the experimentally accessible range. For PCBCF₃, both electrodes gave similar ϵ_r that were lower than PCBM, which is expected from the reduced polarizability of the $-\text{CF}_3$ group. Conversely, ϵ_r was higher for OEG-functionalized fullerenes, as expected, with PCBDE-OH giving slightly higher value using EGaIn compared to Al. Two compounds, PCBSF and PCBCN, exhibited large differences in ϵ_r between EGaIn and Al. In both cases, the values of ϵ_r were comparable to similar materials (i.e., bearing the same functional groups), but EGaIn gave values closer to the upper bounds. The difference in ϵ_r vanished upon preannealing the PCBSF devices, hinting at a morphological effect that is masked by Al top electrodes. Compounds bearing sulfone groups tend to be glassy and amphiphilic, which can drive self-assembly that affects film roughness.⁴⁷ More studies are needed to understand these differences completely.

Measurements of ϵ_r using EGaIn reproduce the values of PS and other reference materials, establishing that the differences between Al and EGaIn observed in devices comprising PCBSF and PCBCN are not intrinsic to EGaIn. The native Ga₂O₃ layer does not act as an extra capacitor connected in series with the circuit in Figure 1a, as can be seen in the impedance plots, where the Nyquist gives a single semicircle, nor does it add to R_s , which is systematically lower for EGaIn than Al. This observation agrees with the hypothesis of Sangeeth et al. that only a thick layer of Ga₂O₃ grown electrochemically acts as an additional real capacitor.³⁵ Differences in the effective and the geometrical area of the EGaIn, e.g., if EGaIn does not fill the entire volume of the PDMS channel, are not responsible for the differences in ϵ_r because the capacitance is calculated using the geometrical area of the channel, A in eq 3, such that ϵ_r will be underestimated—it would be decreased substantially, not increased.

Having excluded effects specific to using EGaIn top electrodes immobilized in PDMS, we hypothesize that the different values of ϵ_r between EGaIn and Al top electrodes is due to the interface between Al and the film. The deposition of Al requires high temperatures and low vacuum, exposing delicate organic films to hot (and reactive) metal atoms; vapor deposition is a violent and energetic process at the molecular level. While some organic materials tolerate these conditions, others react with Al and/or Al atoms penetrate into the film to a significant degree,²⁰ leading to erroneous values of ϵ_r . The deposition of EGaIn, by contrast, is performed at room temperature, but its shear-yielding rheological properties ensure that it makes stable, conformal contact regardless of the topology, reactivity, or fragility of the organic film; X-ray photoemission spectra of SAMs—which are considerably more delicate than thin films—before and after electrical interrogation with EGaIn top contacts show no damage.³¹ Such a comparison is obviously not possible with Al top contacts.

CONCLUSIONS

Because of the nature of IS and the many variables that affect ϵ_r , it is not possible to claim that one electrode material yields more or less “accurate” values. The vast majority of IS is performed with Al contacts because Al works well for rigid, inorganic materials, and traditional alternatives to vapor deposition are typically laborious and can easily introduce artifacts (e.g., from trapped water, wrinkles, reactivity, etc.). In this paper, we demonstrate the use of EGaIn as an alternative electrode to Al specifically for IS measurements on thin films of organic materials, with an emphasis on OPV. Electrodes

Table 1. Relative Dielectric Constant Values of Materials Comparing Aluminum and EGaIn as Top Electrodes

material	$\epsilon_r \pm \text{SE}$	
	Al	EGaIn
P3HT	3.3 ± 0.1	3.3 ± 0.1
PS	2.6 ± 0.1	2.7 ± 0.1
PCBM	3.9 ± 0.1	3.9 ± 0.1
PCBCF ₃	4.2 ± 0.1	4.3 ± 0.1
PCBDE-OH	5.0 ± 0.1	5.3 ± 0.1
PCBTE-OH	5.0 ± 0.1	5.2 ± 0.1
PCBSF	3.9 ± 0.1	5.1 ± 0.1
PCBSF-ann	5.3 ± 0.1	5.4 ± 0.1
PCBCN	4.1 ± 0.1	5.1 ± 0.1

formed from EGaIn inside microfluidic channels are soft, conformal, nondamaging, and unreactive and are applied at room temperature, eliminating many of the sources of experimental error in the determination of dielectric constants when using thermally deposited electrodes. Moreover, EGaIn electrodes do not require specialized equipment, and the simple design can be incorporated in production lines since the PDMS blocks used to define the microchannels can be removed without damaging the organic films; other electrodes or layers can then be deposited to form a device after characterizing the dielectric properties, eliminating sample-to-sample variation. From the Bode plots, EGaIn devices showed lower values of R_s compared to Al, making the extraction of capacitance more precise in the measured frequency range. The values of ϵ_r calculated for both electrodes were the same for the reference materials and the new fullerene derivatives PCBDE-OH, PCBTE-OH, and PCBCF₃, but EGaIn revealed differences for PCBCN and a sensitivity to annealing (i.e., morphology) that was absent using Al. More studies are needed to understand such subtleties in detail, but the ease of use and accessibility of EGaIn for IS measurements mean that it can be readily taken up by the community.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.8b02212](https://doi.org/10.1021/acs.chemmater.8b02212).

Synthetic details and full characterization data for all new compounds; description of device design and preparation; details of impedance spectroscopy measurements; method of error analysis; atomic force microscopy of films (PDF)

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Notes

The authors declare no competing financial interest.

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